Journal of Molecular Structure 1021 (2012) 147–152

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structural studies of 1-phenyl-2,3-dimethyl-5-oxo-1,2-dihydro-1*H*-pyrazol-4-ammonium 2[(2-carboxyphenyl) disulfanyl]benzoate

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HIGHLIGHTS

- The reaction between 4-aminoantipyrine and 2-mercaptobenzoic acid resulted in a proton transfer salt.
- This compound crystallize in the space group *P*-1.
- The ion-pair units are interlinked by hydrogen bonds forming a ID supramolecular network.
- Spectral studies (IR, NMR, Mass) confirm the formation of proton transfer salt.
- The compound shows thermal stability upto 260 °C.

ARTICLE INFO

Article history:
Received 23 January 2012
Received in revised form 20 April 2012
Accepted 20 April 2012
Available online 28 April 2012

Keywords:
Proton transfer
Aminoantipyrine
Mercaptobenzoic acid
Ion-pair
Crystal structure
Thermal study

ABSTRACT

Reaction of 4-aminoantipyrine with 2-mercaptobenzoic acid afforded a proton transfer derivative, 1-phenyl-2,3-dimethyl-5-oxo-1,2-dihydro-1*H*-pyrazol-4-ammonium 2[(2-carboxyphenyl) disulfanyl]benzoate, ($HAAP^{+}{\cdot}HTBA^{-}$), via the oxidation of 2-mercaptobenzoic acid into 2,2′-dithiobis(benzoic acid). The compound has been characterized on the basis of elemental analysis, IR, ^{1}H and ^{13}C NMR and mass spectral data. The infrared spectrum suggests the existence of an ion-pair compound, which is further established by the single crystal X-ray analysis to be an extended 1D supramolecular chain network extending along 'b' cell direction. The compound shows good thermal stability.

1. Introduction

Among the pyrazolone derivatives, 4-aminoantipyrine (AAP) has been used commonly as reagents in biological [1], pharmacological [2], clinical [3], and analytical applications [4]. Other derivatives of AAP such as schiff bases have been extensively investigated and utilized to construct metal-antipyrine networks in crystal engineering [5]. AAP offers both donor and acceptor sites for hydrogen bonding through amino N atom and keto O atom respectively. These non-covalent interactions play an important role in determining the potential applications of its analogues in material science [6] and pharmaceutical industry [7]. Recent research efforts have shown fascinating molecular topologies and crystal packing motifs due to N—H···O and O—H···O hydrogen bonded interactions in the self-assembly of various amines with carboxylic acids [8,9]. Similar non-covalent interactions leading to supramolecular networks are observed in the self-assembly of 4-aminoantipyrine with salicylic acid [10]. The crystal structure of the resulting compound showed charge assisted hydrogen bond interactions between protonated aminoantipyrine and a deprotonated salicylate anion. This observation prompted us to investigate the interactions between 4-aminoantipyrine and 2-mercaptobenzoic acid (MBA).

Herein, we report our results concerning the spectral and thermal studies along with single crystal X-ray analysis of the proton transfer salt, 1-phenyl-2,3-dimethyl-5-oxo-1,2-dihydro-1*H*-pyrazol-4-ammonium 2[(2-carboxyphenyl) disulfanyl]benzoate, ($HAAP^{+}{\cdot}HTBA^{-}$), obtained during the reaction of 4-aminoantipyrine with 2-mercaptobenzoic acid.

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http://dx.doi.org/10.1016/j.molstruc.2012.04.065

2. Experimental

2.1. Materials and physical measurements

4-Aminoantipyrine (Merck) and 2-mercaptobenzoic acid (Sigma–Aldrich) were of reagent grade and used as such. Microanalysis was carried out using a Vario EL III elemental analyzer. Infra red spectrum was recorded on a Perkin Elmer FT-IR instrument as KBr pellet in the range 4000–400 cm^{-1}. The ^1H NMR and ^{13}C NMR were recorded using Bruker DRX-500 MHz with DMSO as solvent. DART-MS was recorded on a Jeol-AccuToF JMS-T100LC mass spectrometer having a DART (Direct Analysis in Real time) source. The thermal studies were recorded on a Mettler TG-50 thermobalance with a heating rate of 20 °C/min. in nitrogen atmosphere. The single crystal X-ray data-collection of the compound was carried out using Bruker Axs kappa apex 2 CCD diffractometer.

2.2. Synthetic procedure

Refluxing 4-aminoantipyrine (0.203 g, 1 mmol) and 2-mercapto benzoic acid (0.308 g, 2 mmol) in 50% ethanol–water mixture for 15 h, followed by partial room temperature evaporation of the solvent, resulted in the separation of brown colored blocks of the compound, ($HAAP^+ \cdot HTBA^-$) with m.p. 224–225 °C (Scheme 1). The elemental analysis data for the compound, Found(Calcd): C,58.91(58.92); H,4.5(4.55); N,08.15(08.25); S,12.61(12.58) agrees with the empirical formula $C_{25}\ H_{23}\ N_3\ O_5\ S_2$.

2.3. Crystal structure determination of ($HAAP^+ \cdot HTBA^-$)

Single crystal suitable for diffraction was obtained by slow evaporation of a solution of the compound in ethanol–water mixture. The brown crystal of the compound having appropriate dimensions of 0.30 mm × 0.20 mm × 0.20 mm was mounted on a fine-focus sealed tube for X-ray crystallographic study. A Bruker Axs-kappa apex 2 CCD diffractometer equipped with a graphite monochromated Mo Kα ($\lambda = 0.71073$) radiation was used for the measurement of data.

The structure was solved by direct methods and refined by full matrix least squares on F^2 (SHELXL 97) program package [11]. Molecular graphics employed include ORTEP 3 and Mercury 2.3. The hydrogen-atoms potentially involved in hydrogen bonding interactions were located from difference electron density maps. The positions of all H atoms were identified from a difference electron density peak and were fixed geometrically during refinement. The title compound crystallizes in triclinic *P*-1 with $a = 9.6289(2)$ Å, $b = 10.2473(2)$ Å, $c = 13.7889(5)$ Å and $V = 1203.12(6)$ A^3.

The crystallographic XRD data is given in Table 1. Full Crystallographic data (cif file) relating to the crystal structure have been deposited with the Cambridge Crystallographic Data Center as CCDC 764774.

3. Results and discussion

3.1. Single crystal structure of ($HAAP^+ \cdot HTBA^-$)

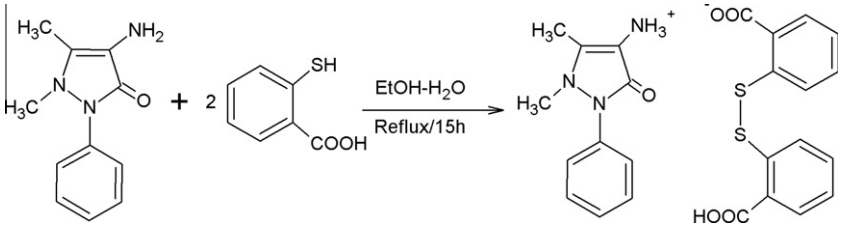
In the present study, during the 1:2 stoichiometric reaction of 4-aminoantipyrine with 2-mercaptobenzoic acid, the acid is first oxidized to 2,2′-dithiobis(benzoic acid), (H_2TBA) [12], which subsequently undergoes proton transfer to 4-aminoantipyrine to form an ion-pair compound, ($HAAP^+ \cdot HTBA^-$). The flexible conformation and variable degree of deprotonation of the dibasic acid (H_2TBA) is known to have formed cocrystals, with few bases, in which the acid–base pairs are held together by charge assisted hydrogen bonds [13].

The compound, ($HAAP^+ \cdot HTBA^-$), crystallizes in the space group *P*-1. The crystal structure reveals the formation of a 1:1 proton transfer compound, held together by a hydrogen bond. Here proton transfer takes place from the carboxyl group at C1 of the dibasic acid, (H_2TBA) to the amino group of the base, (AAP). The asymmetric unit of the compound thus contains 4-ammonium antipyrine, ($HAAP^+$) as the cation and monocarboxylate of 2,2′-dithiobis(benzoic acid), ($HTBA^-$) as the anion (Fig. 1). This is a redetermination of a similar crystalline structure isolated during the direct reaction of 4-aminoantipyrine with 2,2′-dithiobis(benzoic acid) [14].

In the crystal of ($HAAP^+ \cdot HTBA^-$) obtained according to Scheme 1, the pyrazolone ring and phenyl ring are in gauche orientation along the N1—C15 bond. This is reflected from the dihedral angles C23/N1/C15/C20 = −66.0(3)° and C16/C15/N1/N2 = −65.6(3)°. Protonation of the amino group usually leads to the elongation of the C—N bond [15]. This is found true in the case of 4-ammonium antipyrine cation also. The C—N distance [C22—N3 = 1.4270(19) Å] is longer than the C—N distance of neutral AAP (1.3960 Å) [10,16]. This lengthening is observed when the amine N atom of AAP accepts a H atom from the carboxyl group of acid. All other bond length and bond angle values (Table 2) are consistent with those of other reported structure of AAP derivatives.

The anion moiety of the ion-pair is also non-planar. The S1—S2 bond length is 2.0502(6) Å and agrees with the literature value of other disulfides [17]. The dihedral angle value C2/S1/S2/C9 = 83.03(8)° shows that the aryl substituents on the two sulfur atoms are in an approximate perpendicular disposition with respect to each other [12]. The COOH and COO— groups are essentially coplanar with the respective aromatic ring. The benzene ring with COOH group is tilted more from the plane defined by the S1—S2 axis and the respective ring C atoms [S1/S2/C9/C10 = −16.12(15)°] than the other ring with COO— group [S1/S2/C2/C3 = −11.23(15)°]

There are two short non-bonded S···O contacts also [S1···O1 = 2.647 Å and S2···O3 = 2.665 Å] between sulfur atoms of disulphide linkage and oxygen atoms of COOH and COO— groups. The proton transfer from the carboxyl group at C1 to the neighboring amino group of pyrazolone moiety makes the C—C bond joining the COO— group [C1—C7 = 1.493(2) Å] to be slightly longer than that joining the COOH group [C8—C14 = 1.472(2) Å].



Scheme 1.

Table 1
Summary of crystal data and structure refinement for ($HAAP^+ \cdot HTBA^-$).

Empirical formula	$C_{25}H_{23}N_3O_5S_2$	
Formula weight	509.58	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Triclinic, *P*-1	
Unit cell dimensions	a = 9.6289(2) Å	α = 99.803(2)°
	b = 10.2473(2) Å	β = 92.0030(10)°
	c = 13.7889(5) Å	γ = 115.3080(10)°
Volume	1203.12(6)°A^3	
Z, Calculated density	2, 1.407 Mg/m^3	
Absorption coefficient	0.264 mm^{-1}	
F(000)	532	
Crystal size	0.30 × 0.20 × 0.20 mm	
Theta range for data collection	2.25–29.95°	
Limiting indices	$-13 \Leftarrow h \Leftarrow 13$, $-14 \Leftarrow k \Leftarrow 14$, $-19 \Leftarrow l \Leftarrow 19$	
Reflections collected/unique	29812/6936 [R (int) = 0.0294]	
Completeness to theta = 25.00	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.951 and 0.902	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6936/0/320	
Goodness-of-fit on F^2	1.034	
Final R indices [I > 2sigma(I)]	$R1$ = 0.0444, wR2 = 0.1130	
R indices (all data)	$R1$ = 0.0685, wR2 = 0.127	
Largest diff. peak and hole	0.335 and −0.193 e A^{-3}	

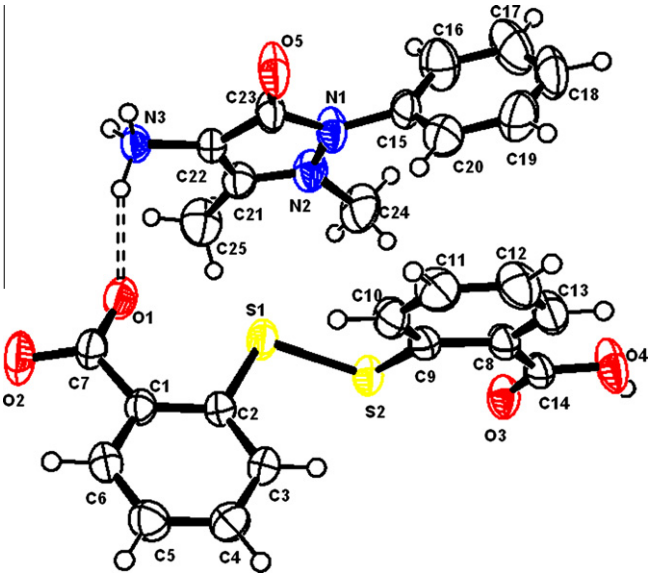


Fig. 1. ORTEP diagram of $HAAP^+ \cdot HTBA^-$.

The cation and anion moieties of ($HAAP^+ \cdot HTBA^-$) are held together by N3—H3A·O1 hydrogen bond (Fig. 1). The presence of NH_3^+ is the source of extensive hydrogen bonds in the lattice (Table 3). Two adjacent inversion related antiparallel ion-pairs are further connected by a pair of N3—H3C·O2 interactions forming a centro-symmetric tetramer. These N—H·O interactions thereby create a R_4^4 (12) motif. The centro-symmetric tetramers then extend along the 'b' cell direction by means of N3—H3B·O3 and O4—H4B·O5 interactions forming $R_2^2(9)$ motifs (Fig. 2). These non-covalent interactions thus form an extended ID supramolecular chain network. Adjacent chains in the crystal structure are held together by van der Waals forces.

Table 2
Selected bond lengths (Å) and torsional angles (°) of ($HAAP^+ \cdot HTBA^-$).

C(1)—C(7)	1.493(2)
C(2)—S(1)	1.7839(16)
C(7)—O(1)	1.227(2)
C(7)—O(2)	1.276(2)
C(8)—C(14)	1.472(2)
C(9)—S(2)	1.7868(17)
C(15)—N(1)	1.418(2)
C(22)—N(3)	1.4270(19)
S(1)—S(2)	2.0502(6)
C(20)—C(15)—N(1)—C(23)	−66.0(3)
C(16)—C(15)—N(1)—N(2)	−65.6(3)
C(3)—C(2)—S(1)—S(2)	−11.23(15)
C(1)—C(2)—S(1)—S(2)	170.20(11)
C(10)—C(9)—S(2)—S(1)	−16.12(15)
C(8)—C(9)—S(2)—S(1)	164.77(12)
C(2)—S(1)—S(2)—C(9)	83.03(8)

Table 3
Hydrogen bond interactions in ($HAAP^+ \cdot HTBA^-$) (Å and °).

D—H···A	d(D—H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
N(3)—H(3A)···O(1)	0.89	1.97	2.8268(19)	160.7
N(3)—H(3B)···O(3)#1	0.89	1.99	2.8552(18)	164.5
N(3)—H(3C)···O(2)#2	0.89	1.67	2.5527(18)	170.7
O(4)—H(4A)···O(5)#3	0.82	1.71	2.5188(18)	168.0

Symmetry transformations used to generate equivalent atoms: #1 $x,y+1,z$ #2 $-x+1,-y+1,-z$ #3 $x,y-1,z$

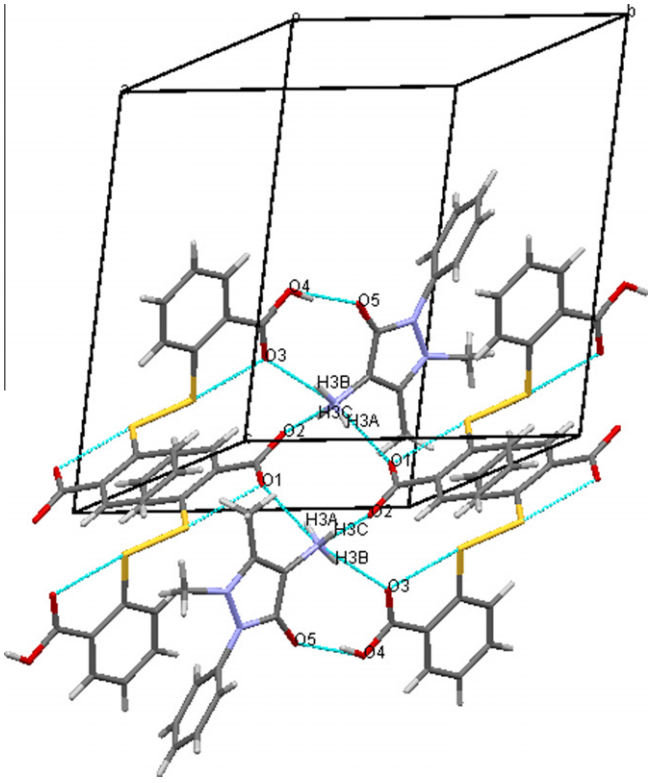


Fig. 2. Hydrogen bond interactions in ($HAAP^+ \cdot HTBA^-$).

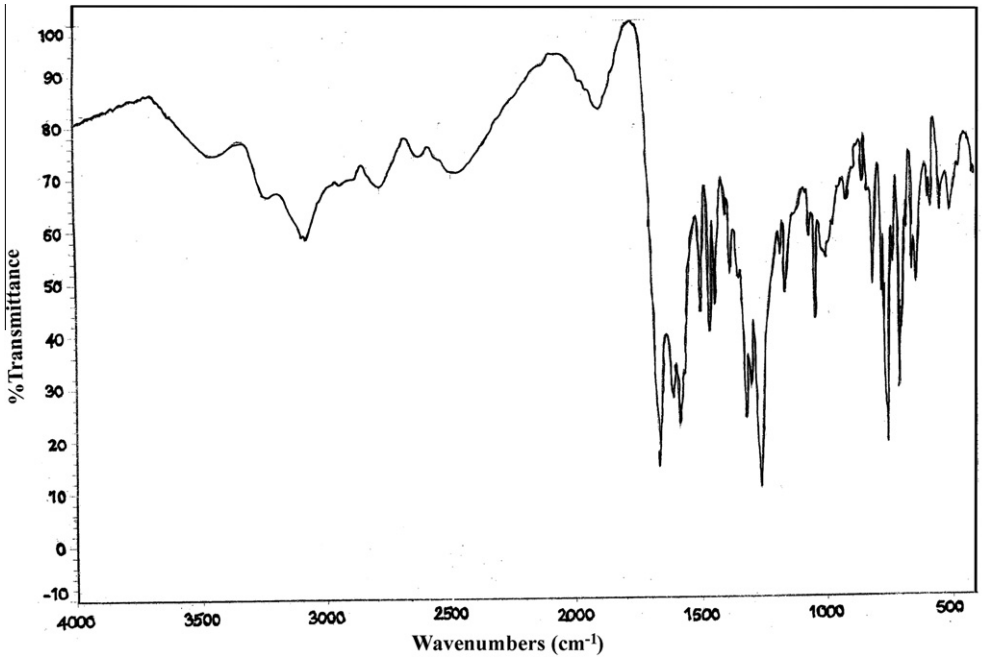


Fig. 3. IR spectrum of ($HAAP^{+}$·$HTBA^{-}$).

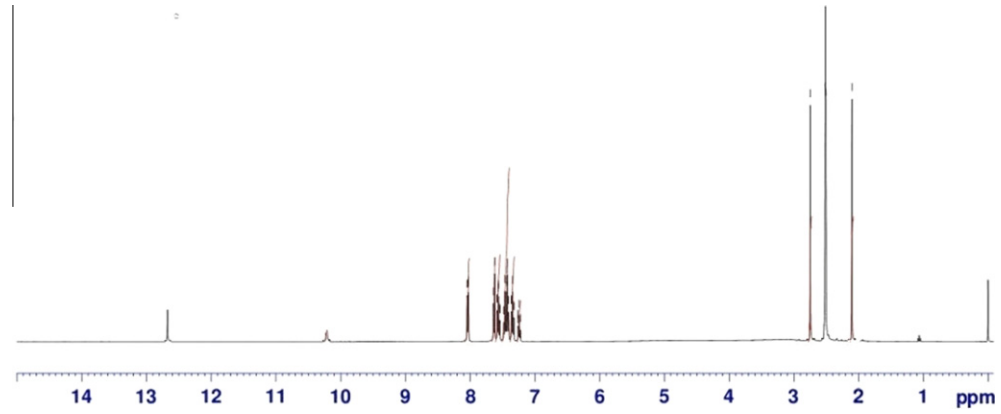


Fig. 4. ^{1}H NMR spectrum of ($HAAP^{+}$·$HTBA^{-}$).

3.2. Spectral studies of ($HAAP^{+}$·$HTBA^{-}$)

The IR spectrum of the compound, ($HAAP^{+}$·$HTBA^{-}$), is characterized by a very strong carbonyl stretching peak at 1664 cm^{-1}, (Fig. 3). It is assigned to the C=O stretch of pyrazole ring which superimposes with the C=O stretch of the carboxylic groups of the acid moiety [18]. A broad band centered at 3231 cm^{-1} is assigned to the stretching of the hydrogen bonded O—H of the COOH group [19]. The O—H bonding frequency appears at 1436 cm^{-1}. The in-plane and out-of-plane stretching modes of O—H are observed at 1261 cm^{-1} and 992 cm^{-1} respectively. A strong peak at 1582 cm^{-1} corresponds to the presence of an ionized carboxylate group. It is further confirmed by the appearance of a weak band at 1372 cm^{-1} due to the symmetrical stretching of COO— [20]. The medium broad band at 1887 cm^{-1} is characteristic of the 1,2-disubstituted benzene rings in the compound. Another intense peak at 749 cm^{-1} supports this observation [21]. In the title compound, NH_3^+ is the source of extensive hydrogen bonding. This is confirmed by the broad ammonium band at 3075 cm^{-1} along with weak bands at 2639 cm^{-1} and 2486 cm^{-1} [22]. The asymmetric and symmetric stretching of N—H bonds are observed at 1608 and 1492 cm^{-1} respectively [23].

A strong band at 1295 cm^{-1} is assigned to ν(C—N)– ν(C—S) and ν(S—S) of the anion is observed at 649 and 549 cm^{-1} respectively [24,25].

The ^{1}H NMR spectra of the compound, $HAAP^{+}$·$HTBA^{-}$ in DMSO (Fig. 4) display two signals of equal intensity at 2.103 ppm (3H) and 2.746 ppm (3H), corresponding to the protons of C—CH_3 and N—CH_3 groups respectively [26]. The aromatic protons give a group of multi signals at 7.222–8.045 ppm (13H). The ammonium protons (NH_3^+) which are involved in extensive hydrogen bonding is observed as a weak broad band at 10.262 ppm [27] whereas the proton of the COOH group is detected at 12.647 ppm [28].

The ^{13}C NMR spectrum of the compound, ($HAAP^{+}$·$HTBA^{-}$) in DMSO (Fig. 5) display the signals corresponding to the different non-equivalent carbons at different values of chemical shift, δ. The methyl carbon atoms of the pyrazol ring appear at δ 9.82 ppm (N–CH3) and 38.18 ppm (C—CH_3). Aryl carbon atoms are observed in the region 119–138 ppm [24]. The carbonyl group of pyrazol ring appears at 161.32 ppm [24]. Due to charge density

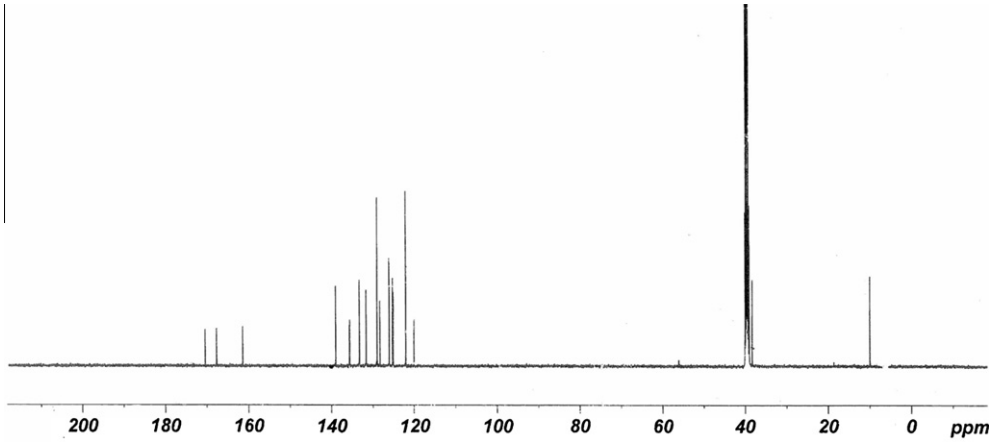


Fig. 5. ^{13}C NMR spectrum of ($HAAP^{+}\cdot HTBA^{-}$).

differences, the carboxylic acid and carboxylate functional groups are having slightly different chemical shift values. The peak at 167.59 ppm corresponds to the carbon atom of carboxylate group [29] and that of carboxylic acid is observed at 170.12 ppm [30].

The mass spectrum of the compound shows a well-defined parent peak at $m/z = 509$, with a relative intensity of 40%. The base peak at $m/z = 204$ is attributed to the cation moiety, $C_{11}H_{14}N_3O$, and the peak at $m/z = 305$ with a relative intensity of 38% is attributed to the anion moiety, $C_{14}H_9O_4S_2$. These observations support the formation of the proton-transfer salt, ($HAAP^{+}\cdot HTBA^{-}$).

3.3. Thermal study of ($HAAP^{+}\cdot HTBA^{-}$)

In order to examine the thermal stability of the new compound, the thermogravimetric analysis of ($HAAP^{+}\cdot HTBA^{-}$) and its parent components, AAP and MBA, were carried out in the temperature range 0–600 °C in nitrogen atmosphere. Comparison of the thermograms revealed that ($HAAP^{+}\cdot HTBA^{-}$) is relatively more stable than AAP and MBA (Fig. 6). The thermal decomposition of ($HAAP^{+}\cdot HTBA^{-}$) commences at 260 °C and continues, without the formation of any thermally stable intermediate, till heating ends at 600 °C. This one step weight loss process confirms that the title compound is a neutral salt, with a remarkably stable hydrogen bonded framework, as evidenced by single crystal X-ray structure [31].

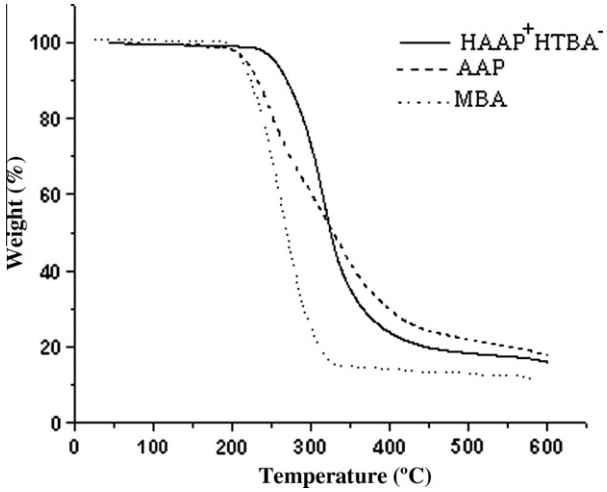


Fig. 6. TGA curves of ($HAAP^{+}\cdot HTBA^{-}$), AAP and MBA.

4. Conclusion

Structural studies of the newly synthesized 1-phenyl-2,3-dimethyl-5-oxo-1,2-dihydro-1*H*-pyrazol-4-ammonium 2[2-carboxyphenyldisulfanyl]benzoate was carried out. Single crystal X-ray analysis of the compound shows the formation of a proton transfer salt, ($HAAP^{+}\cdot HTBA^{-}$). IR, ^{1}H and ^{13}C NMR and Mass spectral data supports the formation of the proton transfer salt. The compound is thermally stable up to 260 °C and then undergoes single stage decomposition. The cation and anion moieties of ($HAAP^{+}\cdot HTBA^{-}$) are held together by various hydrogen bond interactions leading to a 1D chain structure.

Acknowledgments

The authors are thankful to SAIF, IIT Madras for the Single Crystal XRD result and SAIF, Cochin University of Science and Technology, Kochi, India for elemental analysis, IR and NMR studies. Financial aid in the form of research fellowship from University of Kerala (for S.F.), UGC, New Delhi (for A.S.D.) and CSIR, New Delhi (for B.K.B.) is greatly acknowledged.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.04.065.

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